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Urban organic aerosols measured by single particle mass spectrometry in the megacity of London

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Abstract. During the month of October 2006, as part of the REPARTEE-I experiment (Regent's Park and Tower Environmental Experiment) an Aerosol Time-Of-Flight Mass Spectrometer (ATOFMS) was deployed at an urban background location in the city of London, UK. Fifteen particle types were classified, some of which were already discussed (Dall'Osto et al., 2009a,b; Harrison et al., 2012). In this manuscript the origins and properties of four unreported particle types postulated to be due to locally generated aerosols, independent of the air mass type advected into London, are examined. One particle type, originating from lubricating oil (referred to as Ca-EC), was associated with morning rush hour traffic emissions. A second particle type, composed of both inorganic and organic species (called Na-EC-OC), was found enhanced in particle number concentration during evening time periods, and is likely to originate from a source operating at this time of day, or more probably from condensation of semi-volatile species. A third class, internally mixed with organic carbon and sulphate (called OC), was found to spike both in the morning and evenings although it could not unambiguously associated with a specific source or atmospheric process. The fourth class (Secondary Organic Aerosols – Polycyclic Aromatic Hydrocarbon; SOA-PAH) exhibited maximum frequency during the warmest part of the day, and a number of factors point towards secondary aerosol production from traffic-related volatile aromatic compounds. Single particle mass spectra of this particle type showed an oxidized polycyclic aromatic compound signature. A comparison of ATOFMS particle class data is then made with factors obtained by Positive Matrix Factorization and PAH signatures obtained from Aerosol Mass Spectrometer (AMS) data (Allan et al., 2010). Both the Ca-EC and OC particle types correlate with primary Hydrocarbon-like Organic Aerosol (HOA, $R^2 = 0.65$ and 0.50 respectively), and Na-EC-OC correlates weakly with the AMS secondary Oxygenated Organic Aerosol (OOA), ($R^2 = 0.35$). Cluster SOA-PAH was found not to correlate with any AMS signal. A detailed analysis was conducted to identify ATOFMS particle type(s) representative of the AMS cooking aerosol factor (COA), but no convincing associations were found. The combined ATOFMS and AMS results of this REPARTEE study do not always provide an entirely coherent interpretation.

1 Introduction

Tropospheric particles contain a significant and variable fraction of organic material, ranging from 20 % to 90 % of the fine particulate mass (Kanakidou et al., 2005) and divide into two broad categories termed primary and secondary. Primary organic aerosols detected in urban areas are mainly directly emitted from combustion sources, including heavy and light duty vehicles, wood smoke, cooking activities, industries and many others. Once primary particles are emitted they are modified in the presence of various atmospheric oxidants, yielding modified particles with distinctly different chemical

and physical properties compared to their precursor primary particles (Donahue et al., 2009).

Secondary organic aerosols (SOA) are formed from reactions of volatile organic compounds (VOC). SOA consists of a mixture of oxygenated organic species dependent on the degree of processing of the aerosol in the atmosphere, and the precise mechanisms of formation and evolution of SOA are still highly uncertain (Hallquist et al., 2009). The sources and the production mechanisms of primary and secondary organic aerosols represent one of the biggest uncertainties in aerosol science. Models informed by chamber experiments do not always capture the variability of observed SOA loadings, and often predict far less SOA than is observed (Hallquist et al., 2009). This underestimation of SOA strongly suggests the importance of additional pathways of SOA formation not typically studied in laboratory experiments or included in models (Zhang et al., 2007). The chemistry of the formation and continuing transformation of low-volatility species in the atmosphere has been the subject of recent review articles (Kanakidou et al., 2005; Goldstein and Galbally, 2007; Kroll and Seinfeld, 2008). Until recently, organic particulate material was simply classified as either primary or secondary with the primary component being treated in models as nonvolatile and inert. However, the simplified models failed to explain a number of key aspect of the aerosols, including the highly oxygenated nature of ambient OA and the high concentrations of OA during periods of high photochemical activity. Recent studies have shown that semivolatile components of primary aerosols desorb into the gas phase during aerosol transport, thereby undergoing oxidation in the gas phase, leading to SOA formation (Robinson et al., 2007). This opens the possibility that low-volatility gas-phase precursors, including long chain n-alkanes, PAHs and large olefins, are a potentially large source of SOA.

Polycyclic Aromatic Hydrocarbons (PAH) have been identified as a major component in emissions from diesel engines and wood burning sources (Schauer et al., 1999, 2001). The photo-oxidation of these compounds has been shown to yield high molecular weight (MW) oxygenated compounds (Sasaki et al., 1997; Bunce et al., 1997; Wang et al., 2007), which can partition into the particle phase and lead to significant SOA formation (Mihele et al., 2002). Current atmospheric models do not normally include secondary organic aerosol (SOA) production from gas-phase reactions of polycyclic aromatic hydrocarbons (PAHs). Chan et al. (2009) reported a laboratory study of secondary organic aerosol formation from photooxidation of naphthalene and alkylnaphthalenes. Although the gas-phase emissions were dominated by low molecular weight aromatics, these compounds were estimated to account for only 14 % of the SOA formed in the first 3 h of photooxidation. The estimate is consistent with laboratory results of photooxidation of diesel exhaust (Robinson et al., 2007), in which the "known" consisting primarily of single-ring aromatic gas phase precursors, account for at most 15 % of the SOA formed. The contribution of PAH to SOA is still significant after 12 h of oxidation, at which point the SOA from PAH is about twice that from light aromatics (Chan et al., 2009).

Whilst biogenic precursors (predominantly monoterpenes) have traditionally been thought to dominate regional SOA formation, anthropogenic compounds may contribute an appreciable fraction of SOA in urban areas. Mono-aromatic hydrocarbons are one of the most abundant types of organic compound found in the urban atmosphere. Langford et al. (2010) recently reported fluxes and concentrations of volatile organic compounds above central London, estimating that traffic activity was responsible for about 70 % of the aromatic compound fluxes. The ultimate photo-oxidation products of many relatively simple mono-aromatic species remain unknown, due to the complexity and low concentrations formed. The incorporation of a mono-aromatic compound into polymeric structures with acetal polymers was also suggested (Kalberer et al., 2004).

In recent years aerosol mass spectrometry has become available as a powerful tool for the on-line chemical characterization of individual aerosol particles (Murphy, 2007) or small aerosol ensembles (Canagaratna et al., 2007). During the month of October 2006, the REPARTEE-I campaign (Regent's Park and Tower Environmental Experiment) studied atmospheric chemical processes, and particularly those affecting atmospheric aerosol, in London. Two different particle mass spectrometers were deployed: an Aerodyne Compact Time-of-Flight Aerosol Mass Spectrometer (C-ToF-AMS) (Drewnick et al., 2005) and an Aerosol Time-of-Flight Mass Spectrometer (ATOFMS) (Gard et al., 1997). The ATOFMS provides single particle information on the abundance of different types of aerosol particles as a function of particle size with high time resolution, whereas the AMS measures quantitatively mass concentrations of the non-refractory aerosol components as well as species-resolved size distributions (Canagaratna et al., 2007). These types of on-line aerosol analysis instrumentation have greatly advanced our understanding of atmospheric chemistry and climate (Sullivan and Prather, 2005). Whilst the AMS has provided advances in the source apportionment of primary versus secondary organic aerosol components (Canagaratna et al., 2007), the ATOFMS has less adequate source apportionment capabilities due to the difficulties in quantification of its outputs. However, as a main objective of this study, we investigate the temporal trends and the mass spectral features of specific particle types classified with the ATOFMS and we try to deduce chemical and physical aerosol features, attempt a source identification and compare the results with those obtained by using an AMS deployed during the same field study.

A number of papers generated during the REPARTEE experiment have already been published.

This analysis complements the studies of Dall'Osto et al. (2009a) concerning a fog event and of Dall'Osto et al. (2009b) concerning different types of nitrate containing

particles (and their atmospheric behaviour). Table 1 summarizes the 15 clusters found during the REPARTEE I field study. Twelve of the 15 clusters contained mass spectral peaks characteristic of organic containing aerosols, accounting for 83.7 % of the total particles classified (see Table 1). The present study aims to present a detailed analysis of some specific ATOFMS particle classes not described in other studies. The particle types herein described were predominantly organic particle types presenting systematic diurnal trends persisting over three weeks and therefore attributable to local primary and secondary processes occurring daily at the local scale and independent of whichever air mass type the city of London was exposed to. Aspects of the data are compared with the source attribution results for organic carbon derived from PMF analysis of AMS data collected during the same campaign by Allan et al. (2010).

The ATOFMS collects individual particles whilst the AMS collects an ensemble of particles which can be interpreted as a mass concentration of the major non-refractory components. The AMS thus measures the particle mass loading ($\mu g\,m^{-3}$) whilst the ATOFMS temporal trend is reported as the number of particles detected (ATOFMS counts per hour), but the correlation can be very good ($R^2 = 0.75$) (Dall'Osto et al., 2009a). The objective of this study is to look at general organic and inorganic components, but it also aims to present four specific organic particle types occurring during this study, which have not been reported in our earlier papers (Dall'Osto et al., 2009 a,b). Allan et al. (2010) reported a detailed source apportionment analysis of the organic aerosols from REPARTEE based on the AMS: secondary Oxygenated Organic Aerosols (OOA, 53 %), primary Hydrocarbon-like Organic Aerosol (HOA, 25 %) and primary Cooking Organic Aerosol (COA, 22 %) but a comparison with the ATOFMS results was not attempted. The organic mass fragments 55 (*m/z* 55) and 57 (*m/z* 57) are crucial for the identification of COA and HOA, respectively (Allan et al., 2010; Mohr et al., 2012), and particular emphasis is given to identify ATOFMS signals representative of the AMS COA cooking aerosol factor.

2 Experimental

2.1 Aerosol sampling

Sampling took place in Regents Park, one of the Royal Parks of London between 4 and 23 October 2006. Regents Park is located in the northern part of central London. The park has an outer ring road called the Outer Circle (4.3 km) and an inner ring road called the Inner Circle. Apart from two link roads between these two, the park is reserved for pedestrians and the ca. 2 km^2 park is mainly open parkland. The sampling site chosen was inside the inner circle, in an open area usually reserved for parking and gardening purposes. All the instruments were housed in a mobile laboratory. The site was operated as part of the REPARTEE-I experiment (Regent's Park and Tower Environmental Experiment) aiming to study atmospheric chemical processes, and particularly those affecting atmospheric aerosol, in London (Harrison et al., 2012). Meteorological, gas-phase and aerosol measurements were conducted from the top of a 10 m high tower constructed on site. To minimise sampling losses, aerosol was drawn down a sampling stack from which it was isokinetically sub-sampled into a 2 cm diameter stainless steel tube leading to the mobile laboratory. Local meteorological conditions were measured by humidity and temperature probes, and a sonic anemometer which measured the 3-D wind field at the sampling site.

2.2 Instrumentation

The ATOFMS collects bipolar mass spectra of individual aerosol particles. Ambient aerosol is focused into a narrow particle beam for sizes between 100 nm and 3 µm. Using a 2-laser velocimeter particle sizes are determined from particle velocity after acceleration into the vacuum. In addition, the light scattered by the particles is used to trigger a pulsed high power desorption and ionization laser ($\lambda = 266$ nm, about 1 mJ $pulse^{-1}$) which evaporates and ionizes the particle in the centre of the ion source of a bipolar reflectron ToF-MS. Thus, a positive and negative ion spectrum of a single particle are obtained. The mass spectrum is qualitative in that the intensities of the mass spectral peaks are not directly proportional to the component mass but are dependent on the particle matrix, the coupling between the laser and the particle and the shot to shot variability of the laser. However, the ATOFMS can provide quantitative information on particle number as a function of composition; providing a measure of all particle components and can be used to assess mixing state. The ATOFMS provides information on the abundance of different types of aerosol particles as a function of particle size with high time resolution (Gard et al., 1997). Recent studies (Jeong et al., 2011) report excellent correlations between inorganic species (sulphate, nitrate and ammonium) but weaker ones between total organic and elemental carbon detected with ATOFMS and other instruments such as the AMS, the Gas-Particle Ion Chromatograph (GPIC), and the Sunset Lab field OCEC analyzer. However, there are no intercomparisons between specific PMF factors derived from the AMS organic matrix (Ulbrich et al., 2009; Allan et al., 2010) and ATOFMS clustering results.

ATOFMS laser desorption/ionization of chemical species in the particles is accomplished using a Nd:YAG laser operating at 266 nm, and PAHs and their heterocyclic analogues present very high molar absorptivity at this wavelength therefore it is expected that these compounds will be detected among the most easily of all compounds using ATOFMS (Silva and Prather, 2000). The laser fluence of the LDI laser of the ATOFMS was kept very low (0.8–0.9 mJ per pulse) in comparison to other studies (1.3–1.6 mJ). The reason for

Table 1. ATOFMS particle clusters identified from the REPARTEE campaign.

Main	ATOFMS cluster	N particles	% cluster	Particle description
Secondary OA	LRT nitrate	43 516	33.7	Organic nitrogen and nitrate containing aerosols Dall'Osto et al. (2009a)
	LRT core	10 278	8.0	
	Local nitrate	29 563	22.9	
	Amine	2306	1.8	
	HMOC (fog)	4865	3.8	Secondary organic aerosol during fog Dall'Osto et al. (2009b)
	MSA (fog)	245	0.2	
	SOA-PAH	2834	2.2	This study
Primary OA	Ca-EC	5496	4.3	This study
	OC	4671	3.6	This study
	PAH events	269	0.2	This study
	EC	2001	1.5	Coarse Elemental Carbon Long range transport aerosols Dall'Osto et al. (2009a)
Inorganic	Na-OC-EC	2207	1.7	Inorganic particles due to sea salt (NaCl) and Fe (mainly during long range transport)
	NaCl only	3637	2.8	
	Aged NaCl	15 638	12.1	
	Fe	1748	1.4	
	Total	129 274	100.0	

selecting lower laser fluence was to reduce the fragmentation of organic compounds, hence enhancing the detection of high molecular weight species as molecular ions (Silva and Prather, 2000). As a result, a wider variety of particle mass spectra is generated and can provide a better understanding of the different sources and processes occurring in the urban atmosphere.

A Multi-Angle Absorption Photometer (MAAP, Thermo Electron) (Petzold and Schonlinner, 2004) was also used to measure 1-min averages of the ambient black carbon concentrations. Moreover, Dichotomous Partisol-Plus Model 2025 sequential air samplers, fitted with PM_{10} inlets were deployed for collecting fine ($PM_{2.5}$) and coarse ($PM_{2.5-10}$) fractions. A number of other instruments were used during the REPARTEE-I campaign (Harrison et al., 2012) but are not listed here since their data are not discussed in this paper. Local meteorology was determined by a Weather Transmitter WXT510 (Vaisala Ltd, Birmingham) probe. Gas measurements were obtained by Thermo Environment 42CTL chemiluminescence gas analyser with thermal converter and by Thermo Environment 49C photometric UV analyzer for NO_x and ozone, respectively.

2.3 Data analysis

The ATOFMS was deployed at Regents Park for 19 days, between 04/10/06 at 17:00 and 22/10/06 at 23:00. In total, 153 595 particles were ionised by the ATOFMS. The TSI ATOFMS dataset was imported into YAADA (Yet Another ATOFMS Data Analyzer) and single particle mass spectra were grouped with Adaptive Resonance Theory neural network, ART-2a (Song et al., 1999). The parameters used for ART-2a in this experiment were: learning rate 0.05, vigilance factor 0.85, and iterations 20. Further details of the parameters can be found elsewhere (Dall'Osto and Harrison, 2006). An ART-2a area matrix (AM) of a particle cluster represents the average intensity for each *m/z* value for all particles within a group. An ART-2a AM therefore reflects the typical mass spectrum of the particles within a group. The ART-2a algorithm generated 306 clusters used to describe the dataset. By manually merging similar clusters (Dall'Osto and Harrison, 2006), the total number of clusters describing the whole database was reduced to 15. Throughout this paper, an ATOFMS particle type is synonymous with an ATOFMS cluster. It is important to stress the fact that whilst the ATOFMS provides important information on the mixing state of the aerosols and temporal trends of unique particle types over time, the total number of particles sampled by the instrument does not have quantitative meaning without extensive calibrations as it is biased by transmission efficiency (Dall'Osto et al., 2006).

Whilst some semi-quantitative size resolved particle number concentrations of ATOFMS measurements (i.e. Qin et al., 2006) were calculated in this study, a quantification of chemically resolved composition in ambient particles from single particle analyses was not carried out (Jeong et al., 2011).

3 Results

This paper focuses on four particle types named Ca-EC (Calcium-Elemental Carbon), OC (Organic Carbon), Na-EC-OC (Sodium-Elemental Carbon- Organic Carbon) and SOA-PAH (Secondary Organic Aerosols-Polycyclic Aromatic Hydrocarbons) accounting for 4.3 %, 3.6 %, 1.7 % and 2.2 %

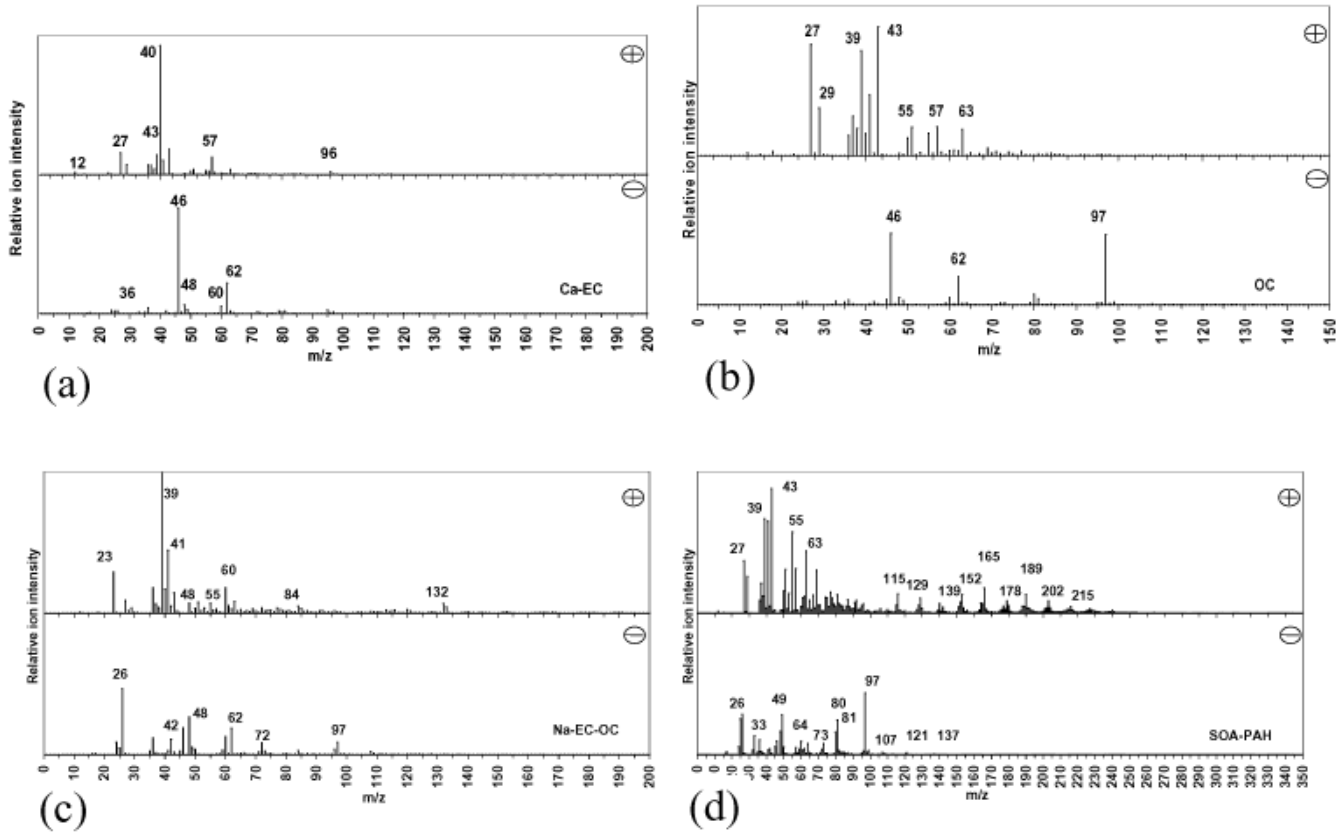

Fig. 1. Positive and Negative ART-2a area vectors attributed to **(a)** Ca-EC, **(b)** OC, **(c)** Na-EC-OC and **(d)** SOA-PAH.

(respectively) of the ATOFMS particles classified during the REPARTEE I experiment.

The weather during the field study was characterized by unusually warm conditions for the month of October in the UK (average temperature $14.1 \pm 2.8\,^{\circ}$C, relative humidity $82.6 \pm 10.7\,\%$; mean ± 1 s.d. of hourly data). The predominant origin of air masses arriving at the receptor was westerly, with Atlantic air masses not strongly influenced by anthropogenic pollution. However, during two periods, air masses arriving at our site from mainland Europe (mainly France and Poland) were detected on 10–11 October 2006 and on 14–20 October 2006. Local wind direction roses were calculated for all 15 ATOFMS clusters, and ATOFMS particle types associated with regional and continental aerosols were found to be associated predominantly with an easterly origin. ATOFMS particle types characterized by daily diurnal profiles were mainly associated with south and east directions, where main roads bordering the Regents Park are located.

3.1 ATOFMS characterization

3.1.1 ATOFMS mass spectra

The positive and negative ART-2a area matrixes for the four particle types described are presented in Fig. 1. The mass spectra of cluster Ca-EC (Fig. 1a) show a strong signature due to calcium (*m/z* 40, 56, 57 and 96), EC (*m/z* −36, −48, −60) and OC (*m/z* 27, 29, 43). Strong signals in the negative mass spectrum are associated with nitrate (*m/z* −46, −62), whereas sulphate (*m/z* −97) is almost absent. This is consistent with a source in vehicle exhaust, which is rich in NO_x but depleted in SO_2 due to use of low sulphur fuel. This particle type has previously been associated with combusted lubricating oil emitted by traffic (Spencer et al., 2006; Toner et al., 2007, Drewnick et al., 2008) and consistently called Ca-EC although in this REPARTEE study a higher signal of nitrate is seen in the negative spectra (Fig. 1a).

Figure 1b shows the ART-2a area matrixes for cluster OC: strong signals due to organic fragments are seen at *m/z* 27, 29, 43, 51, 57 and 63. This particle, by contrast with the Ca-EC type, is internally mixed with both nitrate and sulphate, with a higher signal for the latter. Cluster Na-EC-OC (Fig. 1c) shows a signal at *m/z* 23 for the inorganic component sodium,

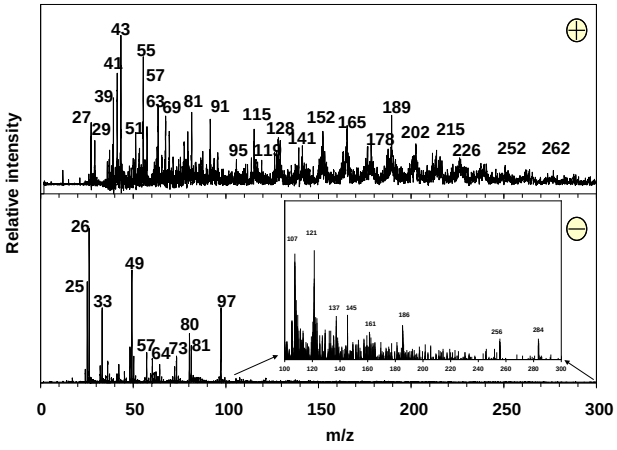

Fig. 2. Single particle positive and negative mass spectra of an individual particle belonging to ART-2a cluster SOA-PAH.

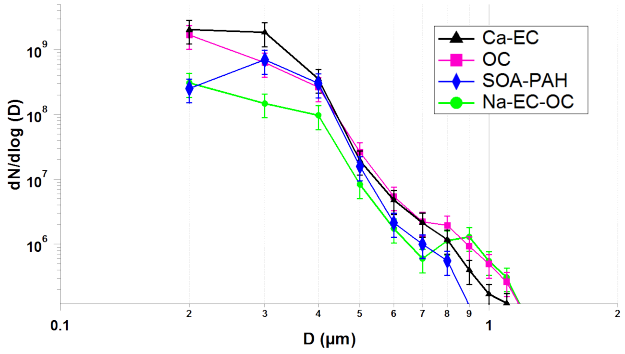

Fig. 3. Size distributions of the 4 ATOFMS particle types described in Fig. 1.

not seen in other mass spectra presented in Fig. 1 and suggesting a different source. Moreover, beside the OC and EC component associated with the Na-EC-OC particle type, the negative spectra of this particle type also show signals due to organic nitrogen (*m/z* −26 [CN] and *m/z* −42 [CNO]).

Cluster SOA-PAH presents a unique positive mass spectrum (Fig. 1d), with strong peaks at *m/z* 27 $[C_2H_3]^+$ and *m/z* 43 $[(CH_3)CO]^+$ usually associated with oxidized secondary organic aerosol (Sullivan and Prather, 2005). *m/z* 51 $[C_4H_3]^+$, 63 $[C_5H_3]^+$, 77 $[C_6H_5]^+$ and 91 $[C_7H_7]^+$ are indicative of a strong aromatic signature (McLafferty, 1993). In the positive mass spectrum, the major peaks at *m/z* above 100 amu show a series at *m/z* 115, 128, 141, 152, 165, 178, 189, 202, 215, 226, 239 and 252 which is usually attributed to PAH compounds (Gross et al., 2000a; Silva and Prather, 2000). Figure 2 shows positive and negative mass spectra of a single particle (aerodynamic diameter 400 nm) belonging to the ATOFMS particle type SOA-PAH. Additional peaks at *m/z* 180, 194, 208, 222, 236, 262 and 276, characteristic of oligomeric species with saturated carbon skeletons separated by Δ14 are present in addition to the PAH series separated by Δ13. Other peaks at *m/z* above 100 can be clearly seen with a series at *m/z* 105, 119, 133 and 147, possibly associated with benzoyl groups and unsaturated or cyclic phenoxy moieties (McLafferty, 1993). The peaks at *m/z* 69, 81 and 95 (particularly the strong peak at *m/z* 95) may represent the exo-sulphur aromatic series (sulphur attached to an aromatic ring) (McLafferty, 1993).

The ATOFMS negative mass spectrum of a single particle from cluster SOA-PAH (Fig. 2) is dominated by *m/z* −25 and *m/z* −26 (likely to be $[C_2H]^-$ and $[C_2H_2]^-$ respectively) and *m/z* at −49 and *m/z* −73 (often found strongly correlated and likely to be related by an unknown fragmentation pattern), which are often associated with fragmentation of PAH and unsaturated organic compounds (Silva and Prather, 2000; Spencer et al., 2006). The presence of strongly acidic compounds is indicated by peaks in the negative spectra. Along with the common peak at *m/z* −97 $[HSO_4]^-$, peaks at *m/z* −80 $[SO_3]^-$, *m/z* −81 $[HSO_3]^-$ and *m/z* −64 $[SO_2]^-$ can be seen. It is interesting to note the minor presence of common peaks due to nitrate (i.e. *m/z* −46 $[NO_2]^-$, *m/z* −62 $[NO_3]^-$ and *m/z* −125 $[H(NO_3)_2]^-$. Perhaps the most interesting feature of the negative mass spectrum of Fig. 2 is the presence of other oxygenated aromatic rings indicated by peaks not reported before in ATOFMS mass spectral characterization seen at *m/z* −107, *m/z* −121 and *m/z* −137, characteristic of fragmentation patterns often associated with flavonoids (Cuyckens and Claeys, 2004; Maul et al., 2008). By querying the whole ATOFMS dataset (about 150 000 single particle mass spectra), it was found that *m/z* −107, *m/z* −121 and *m/z* −137 were unique to this particle type. In summary, the positive and negative ATOFMS mass spectra of particle type SOA-PAH indicate an oxidised organic aerosol component internally mixed with acid sulphate species, along with a complex signature at higher *m/z* which is attributable to high molecular weight polyaromatic compounds.

3.1.2 ATOFMS size distributions

ATOFMS size distributions were obtained by scaling the ATOFMS particle number counts with particle number size distributions to calibrate inlet efficiencies (Qin et al., 2006). It should be stressed that the size distributions presented in this work have only semi-quantitative meaning, as the ATOFMS efficiency is different for different particles and each broad type of particles exhibits a different hit rate (Dall'Osto et al., 2006; Reinard et al., 2007). Whilst the ATOFMS measures precisely the vacuum aerodynamic diameter of individual particles (0.01 μm resolution), particles were summed between 200 nm and 3500 nm at 100 nm intervals for simplification. Figure 3 shows the size distributions for the four ATOFMS particle types Ca-EC, OC, Na-EC-OC and SOA-PAH. Clusters Ca-EC and OC show uni-modal

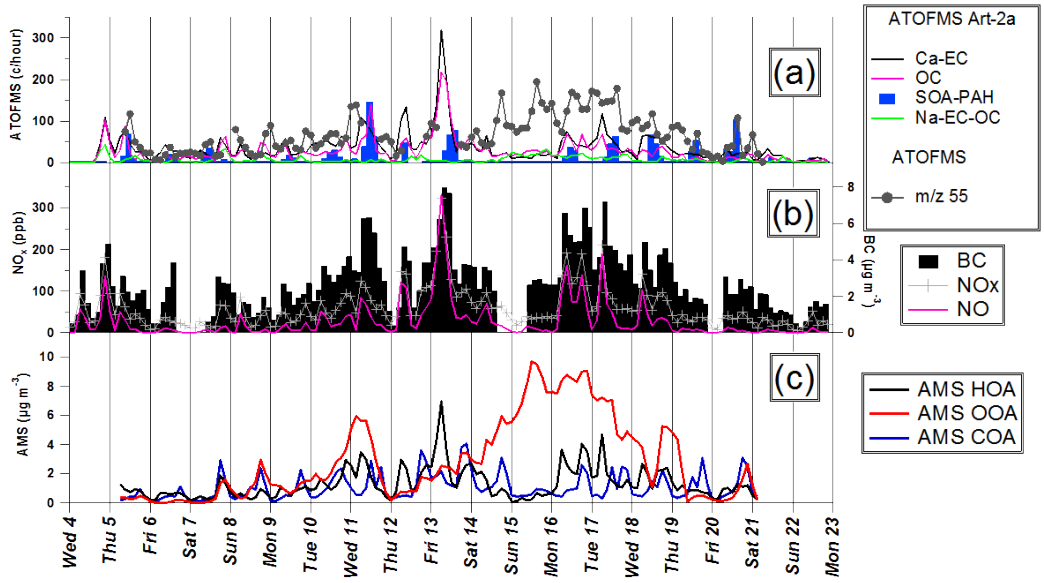

Fig. 4. Temporal trends of **(a)** ATOFMS clusters described in Fig. 1, **(b)** BC and nitrogen gases and **(c)** AMS profiles as reported in Allan et al. (2010).

distributions peaking in the smallest detectable ATOFMS particle diameter at about 200 nm. Previous ATOFMS findings point to primary combustion particles peaking at the smallest detectable ATOFMS particle diameter, whilst more aged secondary organic components (i.e. long range transport organic aerosol) are more typically distributed in the accumulation mode at around 500 nm (Sullivan and Prather, 2005). However, secondary formation close to source could also lead to this size-association. The mass spectra of these two particle types described in Sect. 3.1.1, along with the size distributions herein presented, are suggestive of a primary origin of these particles.

Cluster Na-EC-OC also shows a mode peaking at the smallest sizes, but much less pronounced relative to clusters Ca-EC and OC. By contrast to the first three clusters presented so far, cluster SOA-PAH shows a mode peaking at about 350 nm and not peaking at the smallest detectable ATOFMS particle diameter. The average size distribution of cluster SOA-PAH is shifted towards the accumulation mode relative to clusters Ca-EC and OC and suggests a different origin not related to primary emissions.

3.2 Time trend analysis

3.2.1 Overview of the temporal trends

The temporal trends (3 h resolution) of the four ATOFMS clusters are presented in Fig. 4. Clusters Ca-EC and OC (Fig. 4a) showed maximum abundance during the morning of 13 October 2006, when low wind speed was associated with stagnant conditions, also reflected in high concentrations of primary traffic related species (BC, NO, NO_x, Fig. 4b). Figure 4c shows the temporal profiles of the 3 PMF factor components of the AMS organic matrices described in Allan et al. (2010). The AMS OOA component dominated the periods of 10–12 and 14–20 October 2006 affected by continentally influenced air masses, in which the ATOFMS showed nitrate internally mixed with elemental carbon and organic carbon (Dall'Osto et al., 2009a). AMS factor HOA shows its maximum on the morning of 13 October, and other high concentrations during the morning rush hours of 11, 12, 16 and 17 October, correlating with the maximum values of ATOFMS cluster Ca-EC related to primary traffic emissions (Fig. 4a–c). The highest concentrations of cluster SOA-PAH (Fig. 4a) occurred on 11 and 17–20 October, which are also the days where AMS cluster COA presents its higher mass loading concentrations during daytime (Fig. 4c).

3.2.2 Diurnal profiles

The temporal variability derived from a number of other instruments appear in Fig. 5, showing the average diurnal profiles of (a) ATOFMS clusters described in Fig. 1, (b) AMS PMF factors as reported in Allan et al. (2010); (c) ozone, NO_x and BC concentrations; (d) relative humidity and temperature and (e) ATOFMS single particle mass spectra with *m/z* 55 (absolute peak height > 100). ATOFMS Cluster Ca-EC, as expected from its mass spectra and size distribution, exhibits a maximum during morning rush hours (05:00–09:00) due to primary traffic emissions (Fig. 5a). It shows the same traffic rush hours peaks as NO_x and BC (Fig. 5c), along with the primary organic aerosol traffic related HOA (Fig. 5b) derived by the AMS (Allan et al., 2010). During rush hours BC concentrations were around 4 μg m^{-3}, NO_x

concentrations about 20 ppb, and HOA about 1.5 μg m^{-3}. A second peak at about 16:00 due to the second traffic rush hour period is evident in Fig. 5 for the ATOFMS cluster Ca-EC and NO_x diurnal trends. Cluster OC (Fig. 5a) also showed a spike in the morning traffic rush hour, reflected by a good correlation with cluster Ca-EC ($R^2 = 0.7$). However, cluster OC also exhibited a second sharper peak during evening hours spiking at about 21:00. Cluster Na-EC-OC did not show as strong a diurnal profile as the previous classes described (Fig. 5a) but a two-fold increase occurred between 18:00 and 24:00 relative to the other hours of the day suggesting an additional evening aerosol source or atmospheric process responsible for this particle type. Figure 5a shows that in contrast to the other three ATOFMS particle types presented so far, ATOFMS particle type SOA-PAH exhibits a peak in the middle of the day. An earlier mode starts at about 08:00, as temperature also rises (Fig. 5d) and lasts for about 3 h. A second mode, peaking at 12:00 and 13:00 is in the hottest part of the day. Concentrations decrease substantially after 14:00, disappearing by about 19:00 (Fig. 5a).

The diurnal profile of particles detected by the ATOFMS containing a peak with significant signal (absolute peak height > 100; Gross et al., 2000b) at *m/z* 55 (key peak the COA in the AMS PMF analysis) is also shown in Fig. 5d but is discussed in Sect. 4.2.

3.2.3 Weekday-weekend trend

Average mean values (±1 standard deviation) of the weekday-weekend (WD-WE) variation were calculated for all 15 clusters derived from the ca- 150 000 single particles detected during the REPARTEE-I campaign. The two clusters with the highest weekday to weekend ratio were found to be cluster Ca-EC (weekdays: 16 ± 15; weekend: 8 ± 6; average ATOFMS counts/hour) and cluster SOA-PAH (15 ± 25; 3 ± 7). Whilst clusters Ca-EC and cluster SOA-PAH were found to be two independent groups significantly different from one another (t-test, 95 % confidence), cluster OC (12 ± 17, 9 ± 7) and cluster Na-EC-OC (4 ± 3, 4 ± 5) did not show any statistically significant WD-WE oscillation. A WD-WE analysis of other measurements was also performed in order to compare them with the variation of the ATOFMS clusters. An analysis of the particulate mass loading available for 3 different sites within London during the REPARTEE I campaign (park site "Regents Park" – RP, road site "Marylebone Road" – MR – and 160 m tower "BT tower" – BT –, see Harrison et al., 2012) was carried out, but 16 October 2006 was removed as it exceeded 50 μg m^{-3} largely due to regional pollutant transport and was not comparable with the other days of the month of October 2006. $PM_{2.5}$ at the Marylebone Road air monitoring site showed a strong WD-WE variation (26 ± 7, 20 ± 7; μg m^{-3}, significantly different – t-test, 95 %), whereas the background sites of RP (10 ± 6, 10 ± 7; μg m^{-3}) and BT (10 ± 8, 10.5 ± 9; μg m^{-3}) showed similar values for weekdays and weekend. However, whilst $PM_{2.5}$ at RP did not show a WD-WE variation, traffic markers showed a strong gradient between WD and WE periods (all statistically different, t-test 95 %), including BC (3.2 ± 1.7, 1.8 ± 0.9; μg m^{-3}), NO (36 ± 52, 9 ± 14; μg m^{-3}) and NO_x (70 ± 54, 35 ± 22; μg m^{-3}).

4 Discussion

4.1 Possible source attribution

The Cluster Ca-EC has previously been associated with primary traffic-related combustion particles in both laboratory (Toner et al., 2006), and field measurements (Dall'Osto et al., 2009b, Toner et al., 2008), and this study is in agreement with its primary origin from vehicular emissions. Traffic markers such as NO_x and BC show good correlation with cluster Ca-EC ($R^2 = 0.85$ and 0.7, respectively). Cluster OC presents features pointing towards a primary organic source, similar to cluster Ca-EC; it shows a strong organic carbon signature, a small aerodynamic diameter and peaks in the morning rush hour. However, the cluster OC was internally mixed with sulphate and was elevated also in the evening time. This suggests an additional source occurring in the evening, unlike the cluster Ca-EC which decreases during the evening. Cluster Na-EC-OC showed a broader size distribution with a greater proportion of coarser particles and a mass spectrum internally mixed with inorganic species including sodium and nitrogen, peaking during evening hours. Whilst this particle type contains the strongest peak at *m/z* 39, we exclude a biomass origin for a number of reasons. The peak at *m/z* 39 is not only associated with potassium ($[K]^+$ – to which the ATOFMS is especially sensitive), but may also be due to an organic fragment $[C_3H_3]^+$ (Silva and Prather, 2000). The complete absence of common peaks associated with the presence of potassium (i.e. *m/z* 113 $[K_2Cl]^+$ or *m/z* 213 $[K_3SO_4]^+$) and a ratio between *m/z* 39 and *m/z* 41 of about 18 (the isotopic ratio $^{39}K/^{41}K$ is 13.28) strongly suggest that the *m/z* 39 peak is not due to potassium alone, whereas it dominates in biomass combustion particle types, along with other potassium clusters (Silva et al., 1999). This particle type could originate from a number of sources occurring during the evening times but may also arise from physical processes occurring in the atmosphere during evening time when air temperature falls. A concentration in the evening may also increase due to the contraction of the boundary layer. A previous study showed that during the summer of 2003, an ATOFMS was deployed in another European capital (Athens, Greece: Dall'Osto and Harrison, 2006) and most of the carbon-containing particles appeared to be a secondary product of atmospheric chemistry. In particular, one specific class peaked every night at 22:00, when lower temperature and increased RH values favoured condensation. The secondary particles showed clear internal mixing of organic and inorganic constituents in contrast to their common theoretical

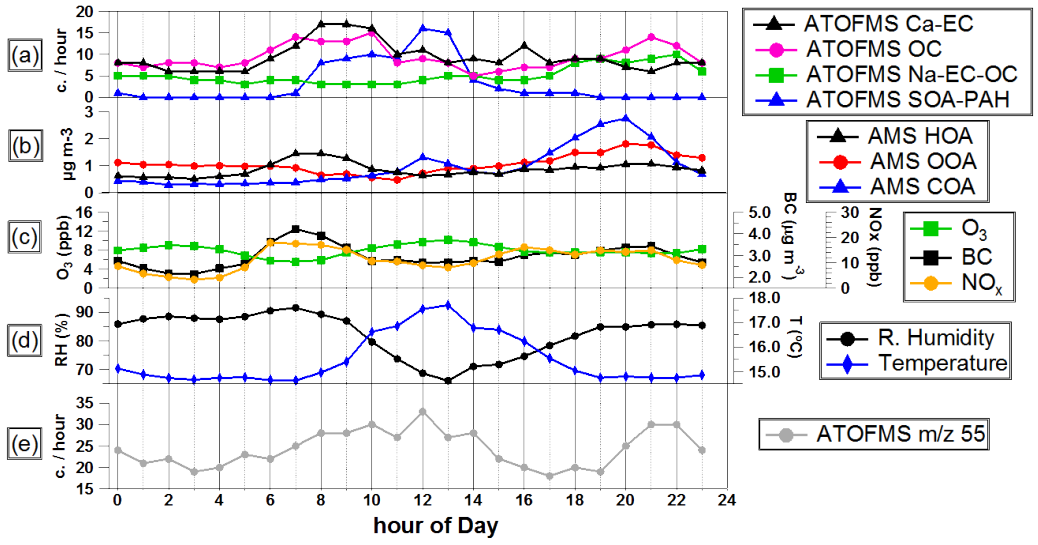

Fig. 5. Average diurnal profiles for **(a)** ATOFMS cluster described in Fig. 1, **(b)** AMS PMF factors as reported in Allan et al (2010); **(c)** ozone, NO_X and black carbon concentrations; **(d)** relative humidity and temperature and **(e)** ATOFMS hit particles with *m/z* 55 (peak height >100).

treatment as external mixtures. The cluster Na-EC-OC from this London field study shows similar mass spectral features as particle types detected in Athens and attributed to condensation of organic compounds onto the particle phase as air temperatures fall.

The cluster SOA-PAH exhibits a unique set of properties, including weekday-weekend variation, maximum frequency during the warmest part of the day, and a mass spectral signature associated with PAH and oxygenated high molecular mass compounds. The fact that cluster SOA-PAH is detected predominantly during weekdays and presents a maximum during the midday hours suggests a photochemical mechanism linked with volatile organic compounds (VOC) arising from traffic activity. The weekday-weekend trend also suggest an anthropogenic source. The mass spectrum of cluster type SOA-PAH was compared with the ATOFMS particle mass spectral libraries. Source signatures, or mass spectral "fingerprints", were obtained by using ATOFMS data from a variety of sources (Toner, 2008). Cluster SOA-PAH did not match exactly any of the 20 different ART2a clusters representative of different cooking related sources, nor any oil, gasoline or diesel combustion source. Finally, it is important to note the absence of any peak associated with common metals (i.e. Ca, Na, K, V) detected in ATOFMS mass spectra of particles originating from primary anthropogenic aerosol sources. The ATOFMS mass spectrum shows signals usually associated with PAH components already described in Sect. 3.1.1, which point to a primary aerosol source. However, the PAH signature may be related to secondary components, possibly oxidation products of PAHs. Reactions of degradation products may also lead to further secondary compounds. Webb et al. (2006) for example showed the organic aerosol product formed from the photo-oxidation of o-tolualdehyde contained a diverse range of chemical functionalities including mono-aromatic, carboxylic and carbonyl groups which were inferred to be photochemical by-products but around 3 % of the organic content resolved was polycyclic aromatic (PAH) in nature. The ATOFMS is very sensitive to polycyclic aromatic structures, so whilst PAH may be a minor component of the mass of the particle, they can generate a disproportionate fraction of the mass spectral signature. The cluster SOA-PAH does not behave as a typical semi-volatile species whose concentration increases as temperature decreases. The fact that its temporal trend does not correlate with any commonly identified primary aerosol components or markers (Ca-EC from ATOFMS, BC, NO_X, SO_2) excludes a primary aerosol source, and the maximum intensity at noon points towards a photochemical origin. Whilst PAHs are emitted directly from combustion processes, the sources of oxygenated PAH emissions in the atmosphere can be both by direct emission and tropospheric conversion of PAHs, but quantitative data on the importance of secondary versus primary origins are scarce (Walgraeve et al., 2010). Ning et al. (2007) reported the daily variation in chemical characteristics of urban secondary ultrafine aerosols, showing that afternoon concentrations of oxygenated organic acids and sulfate rose relative to primary organic compounds in the morning and demonstrating that secondary photochemical reactions are a major formation mechanism of ultrafine aerosols in the afternoon. Specifically, the larger decrease in the concentration of non-oxidized PAHs and alkanes compared to CO in the afternoon indicated their possible volatilization and photo-oxidation in addition to dilution. Verma et al. (2009) suggested in a subsequent study

that the photochemical transformation of primary emissions during atmospheric aging enhances the toxicological potency of primary particles in terms of generating oxidative stress and leading to subsequent damage in cells. Our results are suggestive of secondary reactions modifying the primary organic particles emitted in the morning rush hour.

4.2 Comparison with the on-line AMS findings

The AMS instrument provides invaluable quantitative information upon the aerosol mass loading of generic organic components. In the last decade, the AMS non-refractory organic components have been sub-divided into two broad groups: hydrocarbon-like and oxygenated organic aerosol (HOA and OOA, respectively) (Canagaratna et al., 2007). Recently, Positive Matrix Factorization (PMF) has been demonstrated to be a powerful tool for the purposes of profiling different components of the ambient organic aerosol data matrix from the AMS. Lanz et al. (2007) and Ulbrich et al. (2009) for example reported a third AMS component: a less-oxygenated (relative to the factor OOA), semi-volatile organic aerosol that correlates well with nitrate and chloride. During this REPARTEE I experiment, Allan et al. (2010) reported a detailed analysis of the AMS organic aerosol component sampled during the REPARTEE-I campaign, reporting three components: HOA (25 %), OOA (53 %) and a factor associated with primary organic aerosols related to cooking emissions COA (22 %). This COA factor has also been recently reported in other large megacities (Huang et al., 2010; Sun et al., 2011) but not compared with any other on-line instrument. In this study we attempt to compare the AMS PMF factors (with particular emphasis on the COA) seen by the AMS with the on-line measurements taken with the ATOFMS. Not only are ATOFMS particle type mass spectra correlated with the AMS factors, but also the temporal trend of a specific *m/z* peak (55, a *m/z* peak characteristic of the COA AMS factor) is also studied. A comparison between the ATOFMS and the AMS is not straightforward, as the qualitative temporal information of the ATOFMS particle number concentration of single particle mass spectral type does not allow a meaningful correlation with quantitative aerosol mass loading concentrations of organic components provided by the AMS. A correlation coefficient (R^2) matrix between ATOFMS particle types (number) and AMS mass concentrations appears in Table 2.

A brief analysis of the primary organic aerosol components described in detail in Allan et al. (2010) showed the traffic HOA component to present a strong WD-WE difference: $1.3 \pm 0.8\,\mu g\,m^{-3}$ and $0.6 \pm 0.5\,\mu g\,m^{-3}$ (respectively) reflecting the BC and NO_x difference of about a factor of two higher during weekdays. Factor COA did not show statistically significant variation, ($1.4 \pm 1.1\,\mu g\,m^{-3}$ and $1.2 \pm 0.9\,\mu g\,m^{-3}$, for WD and WE, respectively). However, given the fact that AMS factor COA presents two peaks at about 12:00 and 20:00, further separation was required. Factor COA was divided into WD-WE periods, further split between day time (09:00–18:00) and evening time (18:00–24:00). COA-day was found to be about 25 % higher during weekdays ($1.03 \pm 0.78\,\mu g\,m^{-3}$) relative to weekend ($0.76 \pm 0.41\,\mu g\,m^{-3}$), statistically different (t-test, 95 %). HOA presented overall statistically significant lower values over weekend periods for both day and evening, with the former reduced more (about 60 %) than the latter (about 20 %).

4.2.1 Comparison with the AMS PMF factors

ATOFMS cluster Ca-EC, as well as cluster OC, correlate with the AMS HOA ($R^2 = 0.65$ and 0.50 respectively), as shown in earlier studies (Drewnick et al., 2008). The AMS factor OOA represents a well-aged secondary organic aerosol, and was found to be consistent with an atmospheric regionally transported source rather than local meteorology, as reported in Dall'Osto et al. (2009a). It correlates weakly with particle type Na-EC-OC. Beside the commonly measured HOA and OOA factors, a further component, COA exhibited a unique mass spectrum with strong signals at *m/z* 41 and *m/z* 55. However, as noted by Allan et al. (2010), the 3 factor solution approach tended to result in residuals larger than would be considered optimal according to the error model, which indicates that the number of factors used is insufficient to capture all of the chemical variability within the dataset. However, the fourth factor solution generated some splitting of PMF factors and therefore the three factor solution was kept.

This implies that the 3 factor solution is masking some additional information but the variability is not enough to justify the 4 factor solution or additional sources of organic aerosols rather than the three (HOA, OOA and COA). *m/z* 55 (a marker of COA) was found to have large variability (Allan et al., 2010) but a 4-factor solution could not be justified.

The ART-2a analysis on the ATOFMS dataset did not reveal any specific particle type associated with cooking activities. However, some peaks usually attributed to cooking activities (Rogge et al., 1993) were found in cluster SOA-PAH. Figure 2 shows peaks at *m/z* −256 (thought to be hexadecanoic acid) and *m/z* −284 (octadecanoic acid). Ning et al. (2007) reported ultrafine particles sampled in the afternoon in Los Angeles to contain more organic matter than the morning samples (more SOA), to be more acidic (less ammonia to neutralize the sulphuric acid), and to be rich in octadecanoic acid and hexadecanoic acids. Whilst Rogge et al. (1993) showed that food cooking is a source of organic acids, it was concluded that atmospheric chemistry (oxidation of VOC precursor gases) is more likely responsible for their formation as food cooking alone cannot explain the atmospheric concentrations measured (Pandis et al., 1993; Rogge et al., 1993). However, far fewer published profiles are available for food cooking relative to motor vehicles and biomass combustion, and significant inconsistencies exist between the ambient data and published source profiles

Table 2. Correlations (R^2) between ATOFMS organic particle types (number) and AMS concentrations averaged over 3-h intervals.

3 h resolution	AMS OOA	AMS HOA	AMS COA	AMS org
ATOFMS Ca-EC	< 0.1	0.65	< 0.1	0.12
ATOFMS OC	< 0.1	0.50	< 0.1	0.14
ATOFMS Na-EC-OC	0.35	-0.1	< 0.1	0.14
ATOFMS SOA-PAH	< 0.1	< 0.1	0.15	< 0.1
AMS PAH	< 0.1	0.45	0.44	0.3
AMS PAH low	< 0.1	0.28	0.55	0.25
AMS PAH high	< 0.1	0.58	0.16	0.35

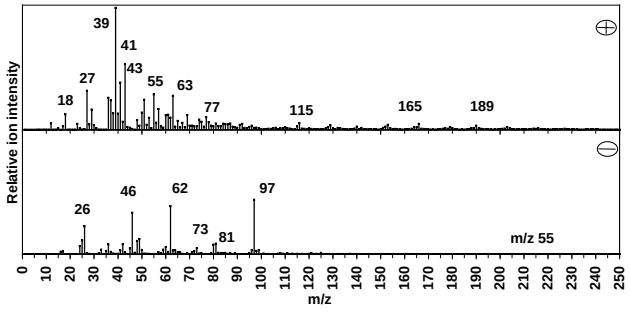

Fig. 6. Average mass spectra for all hit particles during the REPARTEE I campaign containing values of peak height at *m/z* 55 higher than 100.

so further studies are required in order to correctly apportion food cooking emissions (Robinson et al., 2006). Furthermore, it is important to note that earlier work on the identification of cooking sources has mainly been focused on meat cooking and barbeque sources, rather than vegetable oils.

The ATOFMS and the AMS mass spectra contain different fragmentation patterns (Murphy et al. 2007, Canagaratna et al., 2007). In the ATOFMS, *m/z* 55 is usually seen in organic aerosol with aromatic compounds (Prather and Sullivan, 2005) but a comparison between the same *m/z* seen by the two different instruments was still attempted. By querying all the ∼150 000 ATOFMS single particle mass spectra containing a peak at *m/z* 55 (peak height >100), a key peak describing the third AMS factor (COA) solution (Allan et al., 2010), 11 500 particles were found with such peak. Figure 6 shows the average ATOFMS mass spectra of particles containing a peak at *m/z* 55 (from here called particle type *m/z* 55). This peak does not seem to appear in inorganic particle types (Table 1). The average mass spectrum shows peaks due to OC (*m/z* 27, *m/z* 41, *m/z* 55, *m/z* 63, *m/z* 77), fragments of large aromatic compounds (*m/z* 115, *m/z* 165), nitrate (*m/z* −46, *m/z* −62) and sulphate (*m/z* −97), all peaks contained within particle types OC, Na-EC-OC and SOA-PAH. The broad similarity of the mass spectra shown in Fig. 6 with particle types OC, Na-EC-OC and SOA-PAH is also reflected in the fact that the total number of particles containing *m/z* 55 broadly follows the sum of the 3 ATOFMS Art-2a clusters (Fig. 4). The temporal trend of particle type *m/z* 55 in Fig. 5e, where a bimodal diurnal profile can be seen peaking at noon and during evening times bears some similarity to the COA factor, but the correlation between the sum of the three ATOFMS types (OC + Na-EC-OC and SOA-PAH) and AMS factor COA is entirely insignificant ($R^2 < 0.1$) (Table 2). It does however raise the question over whether the COA factor is comprised of a number of different particle types arising from different sources. The two instruments involve very different vaporisation/ ionisation procedures (ATOFMS by u.v. laser and AMS by heating and electron impact) probably leading to significantly different mass spectral fragmentation patterns in terms of relative peak intensities, if not *m/z* values. The cooking aerosol may be transparent to the u.v. laser, hence failing to ionise in the ATOFMS. The ATOFMS analyses individual particles and therefore sees a particle resulting from coagulation as different from its two parent particles whereas the AMS views an aggregate mass spectrum of particles of all types admitted to the instrument at a specific time. It should also be remembered that the two instruments are responsive to different particle size ranges and that the cooking oil aerosol characterised as the COA factor by the AMS may be of too small a size (<200 nm) to be seen by the ATOFMS. These differences make it very difficult to try to intercompare data from the two instruments, although sometimes data from one can be valuable in informing interpretation of data from the other (e.g. Dall'Osto et al., 2009a; Drewnick et al., 2008). In this dataset, the ATOFMS does not appear to see any particle type characteristic of a cooking source.

4.2.2 PAH detection by the two instruments and intercomparison

Polycyclic aromatic hydrocarbons (PAHs) are products of incomplete combustion formed during the burning or pyrolysis of organic matter, and are released into ambient air from a wide range of combustion sources (Finlayson-Pitts and Pitts, 2000). Several physical and chemical processes such as gas-phase distribution and transformation reactions determine the levels of PAHs in the atmosphere. PAH transformation products include a wide range of compounds that can be classified as nitro-PAHs and oxygenated PAHs. Because of the high potential mutagenic and toxic effects of oxygenated PAHs

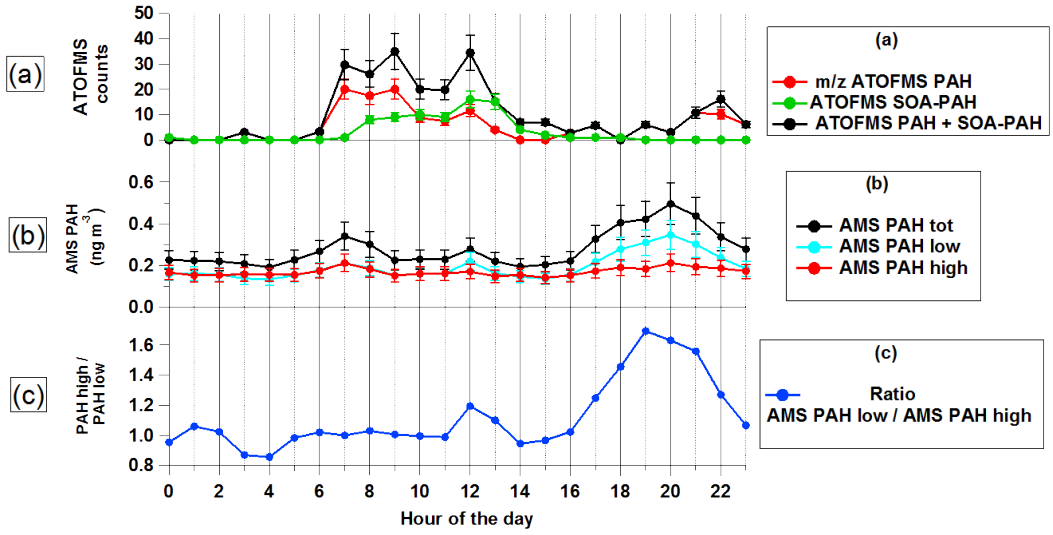

Fig. 7. PAH detection by both ATOFMS and C-ToF-AMS.

(Pedersen et al., 2005), more research on the occurrence, fate and behavior of this group of atmospheric organic micropollutants was recently suggested in the review article of Walgraeve et al. (2010). Quantitative data on the relative importance of secondary versus primary oxygenated PAHs are scarce (Sklorz et al., 2007; Tsapakis and Stephanou, 2007; Albinet et al., 2008). Recently Kojima et al. (2010) suggested that a considerable fraction of some oxy-PAHs associated with PM in downtown Tokyo, Japan originates from atmospheric formation. Walgraeve et al. (2010) reported that the accurate and precise analysis of oxygenated PAHs in atmospheric PM is a challenging multi-step task, including issues with sampling artefacts, solvent extraction techniques and the complex matrix in which trace concentrations of oxygenated PAHs in the atmosphere occur. By contrast, real-time mass spectrometry techniques provide high time resolution for insight into brief events and diurnal changes while eliminating the potential artefacts acquired during long-term filter sampling (Pratt and Prather, 2012).

The ATOFMS has proven successful in detecting PAH, nitro-PAH and oxygenated PAH (Silva et al., 2000). During our study, we found a specific ATOFMS ART-2a cluster particle type rich in PAH, but it presented only 269 particles, distributed during two hours of the field study (during the days of 5 and 12 October) and likely to be due to a local Regent Park gardener vehicle passing by. However, by searching the ATOFMS database for specific PAH peaks (*m/z* 156, 178, 202, 228, 252, 276, Silva and Prather et al., 2000; Gross et al., 2000a), about 2000 particles contained PAH signatures (1.5 % of the total). The diurnal profile of PAH containing particles is shown in Fig. 7a, where a peak can be seen in the morning (07:00–09:00 a.m.) due to traffic rush hours. By contrast, as discussed in Sect. 3.2.2., cluster SOA-PAH starts to rise at 08:00 a.m. to show its maximum occurrence at 12:00–01:00 p.m. The diurnal temporal trends of the ATOFMS particle types shown in Fig. 7a suggests that PAH-containing vehicular traffic exhaust aerosol is followed by a more oxidised aerosol attributed to atmospheric oxidation of gas phase hydrocarbons (cluster SOA-PAH).

PAH concentration calculations on the AMS dataset were also performed according to the procedure described by Dzepina et al. (2007) with an estimated uncertainty of about 35 %. Figure 7b shows the diurnal trend of AMS PAH as AMS PAH low (PAH < *m/z* 200), AMS PAH high (PAH > *m/z* 200) and AMS PAH (AMS PAH low + AMS PAH high). The diurnal profile of AMS PAH shows three peaks: a morning one between 06:00 a.m. and 09:00 a.m. (peaking at 07:00 a.m.), a little sharp one at lunch time (12:00 p.m.) and broader major ones between 06:00 p.m. and 10:00 p.m. (peaking at 08:00 p.m.). When the ratio AMS PAH low/AMS PAH high is calculated (Fig. 7c) an enhancement of PAH low is seen during lunch and evening times. Whilst the evening peak can be due to condensation of PAH in the particle phase, the increment at lunch time suggests a different source of PAH and/or a transformation of the morning vehicular traffic exhaust PAH aerosol.

By providing the mixing state of individual particles, the ATOFMS shows two different types of PAH-containing particles, but it is not possible to know if the oxidized compounds seen in SOA-PAH were produced in the gas phase or in the particle surface. Other studies reported a more rapid decrease in surface versus bulk PAH concentrations during the late morning, suggesting that freshly emitted combustion related particles are quickly coated by secondary aerosol material and may also be transformed by heterogeneous reactions (Marr et al., 2006).

When correlating measurements taken with the AMS and the ATOFMS, only moderate correlations were found

between ATOFMS PAH-containing particles and AMS PAH ($R^2 = 0.3$), whereas higher correlations were found between primary AMS PMF COA and AMS PAH low ($R^2 = 0.55$) and between primary AMS PMF HOA and AMS PAH high ($R^2 = 0.58$), as shown in Table 2.

The correlation between PAH species detected with the ATOFMS and the AMS was only moderate as the ATOFMS did not detect PAH-containing aerosol during night time, perhaps due to the higher relative humidity (Neubauer et al., 1998).

5 Conclusions

This work emphasises that neither the AMS nor the ATOFMS alone is able to give a comprehensive insight into aerosol composition and sources. Our earlier work has demonstrated that in combination they give far greater insights into aerosol behaviour than either technique can alone (Dall'Osto et al., 2009a,b). The AMS has a well proven capability to quantify generic source-related categories of non-refractory aerosol. The ATOFMS gives mass spectral information upon individual particles which, even after clustering particles with similar size distribution and mass spectral characteristics, presents information which can be very difficult to interpret in relation to the sources or atmospheric processing, as is the case with some particle types identified in this study.

The ATOFMS cannot provide quantitative aerosol mass loading concentrations, but its unique strength relies in the fact that it can monitor in real time variations in the single particle composition. Further work is needed in order to attribute mass spectra to particular sources with greater confidence. Comparing laboratory and ambient spectra may not be sufficient to associate a specific mass spectrum to an aerosol source seen in the ambient data, as particles with primary and secondary origins may have broadly similar mass spectra, and particles are modified substantially during atmospheric transport processes. The ATOFMS particle types Ca-EC, which derives from road traffic, and OC, containing organic carbon from primary sources, correlate strongly with the AMS HOA factor. The modest correlation between ATOFMS particle Na-EC-OC and AMS OOA suggests that this is an aged particle type containing mainly secondary organic carbon. ATOFMS type SOA-PAH appears to be a specific component of secondary organic aerosol for which the ATOFMS has high sensitivity, but which does not represent the temporal trends in total secondary aerosol as shown by AMS factor OOA. There is no clear evidence that any ATOFMS particle type, or combination of particle types, corresponds to the AMS COA cooking factor.

PMF analysis on the AMS datasets is revealing new features in the organic components of the aerosols and is proving to be an excellent tool for extracting information from the AMS mass spectra. It is imperative not only to justify PMF solutions mathematically, but also by comparing different AMS PMF solutions with external data such as can be provided by the ATOFMS. This study shows that the urban organic aerosol is complex and unfortunately the correlations between the two mass spectrometers have proven to be rather weak. Experience to date with the ATOFMS suggests that its greatest strength is in the identification of inorganic particles to which the AMS is currently insensitive because of their generally refractory nature. It is a strength of the AMS that the aggregate mass spectrum reveals information on a number of different organic aerosol types, although some doubts still surround the interpretation of results from PMF. Nonetheless, based upon the current deployment, the AMS has yielded far more valuable information on the organic component of the aerosol than the ATOFMS. The strength of the latter instrument in the REPARTEE campaign has been primarily in relation to inorganic aerosol types, i.e. the nitrates (Dall Osto et al., 2009a) and sulphur compounds (Dall'Osto et al., 2009b). It appears very likely that the PMF analysis with the recent High Resolution HR-ToF-AMS (DeCarlo et al., 2006) of organic matrices in the future will generate more than the common 3–4 factors seen with lower resolution AMS mass spectrometers. Nonetheless, we remain convinced that deployment of both instrument types yields insights into aerosol sources and behaviour not available from one type alone.

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